Use of Amido Grignard Reagents in Inorganic Chemistry. Synthesis and X-Ray Crystal Structure of *anti*-[Pd(Cl)(Py)(μ-2,6-Pr^{i}C$_6$H$_3$NH)]$_2$.

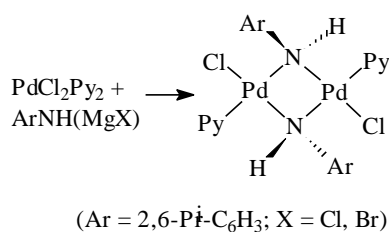Fabio Ragaini,[a] Sergio Cenini*,[a] and Francesco Demartin.[b]

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Graphical Abstract

(Ar = 2,6-Pr^i-C$_6$H$_3$; X = Cl, Br)

Treating a pyridine solution of PdCl$_2$Py$_2$ (Py = pyridine) with a THF or diethyl ether solution of the amido Grignard reagent 2,6-Pr^{i}C$_6$H$_3$NH(MgCl) afforded a dimeric

palladium complex, containing two bridging amido groups, which was structurally characterised.

Abstract

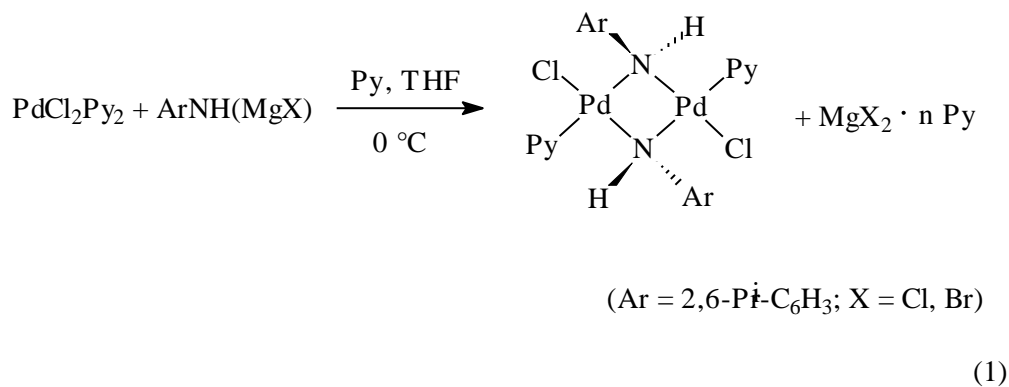Treating a pyridine solution of $PdCl_2Py_2$ (Py = pyridine) with a THF or diethyl ether solution of the amido Grignard reagent $2,6-Pr^iC_6H_3NH(MgCl)$ afforded a dimeric palladium complex, containing two bridging amido groups, which was structurally characterised.

Late transition metal amido and imido complexes, especially those in a low oxidation state, have attracted much attention during recent years since their high reactivity may render them reactive reagents or intermediates in catalytic cycles.[1] Several approaches have been used for the synthesis of these complexes, but the use of the "Grignard" amido reagents $ArNH(MgX)$ (X = halogen) does not appear to have been investigated before. However, the analogous reagent $(THFMgNPh)_6$ has been very recently reported as an imido-transfer reagent for the synthesis of imido complexes of titanium, zirconium and manganese.[2]

Arylamido and imido Grignard reagents have been known for a long time and their use in organic synthesis has been extensively investigated by Okubo and coworkers.[3] Since palladium is probably the most used metal in homogeneous catalysis, we decided to start our investigation from a simple precursor, $PdCl_2Py_2$ (Py = pyridine), in

the hope that following substitution of the labile pyridine ligands of the product may represent a versatile entry to a wide class of complexes.

Treating a pyridine solution of $PdCl_2Py_2$ with a THF solution of 2,6-$Pr^iC_6H_3NH(MgBr)$, generated from the corresponding aniline and EtMgBr, afforded an orange solution and a white precipitate, which was shown by ^1H NMR to contain a mixture of pyridine-containing complexes, but no residue deriving from the anilido fragment. The filtered solution was further treated with *n*-hexane affording a yellow precipitate that, upon standing with the mother solution for two weeks, separated into a white microcrystalline powder and some orange crystals. The orange crystals were suitable for X-rays diffraction and were shown to be constituted by the dimeric amido complex *anti*-$[Pd(Cl)(Py)(\mu$-$2,6$-$Pr^iC_6H_3NH)]_2$, whose structure is shown in Figure 1 (eq. 1):

$$PdCl_2Py_2 + ArNH(MgX) \xrightarrow[0\ °C]{Py,\ THF} \ \ + MgX_2 \cdot n\ Py$$

(Ar = 2,6-Pr^i-C_6H_3; X = Cl, Br)

(1)

→ INSERT FIGURE 1

Palladium amido complexes have attracted much attention as possible intermediates in various reactions and their involvement in the interesting amination of haloarenes[4,5] has been recently proved. Most of the reported complexes are

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mononuclear and only a few dinuclear amido-bridged palladium complexes are known.[6-10] To the best of our knowledge, only in three cases has the crystal structure of a dinuclear palladium amido complex been reported,[7,8,10] although the crystal structure of a trinuclear complex bearing both amido and imido bridging groups has also been reported.[11]

In the crystal, the dimeric complex is located about a crystallographic inversion centre.[†] Both palladium atoms display an almost square planar geometry and are bridged by the two amido ligands and bound to a chloride atom and to a pyridine molecule. The phenyl ring of the amido ligand is almost normal to the plane defined by its nitrogen atoms and by the palladium atoms, for steric reasons. During the structure refinement, the chlorine atom showed an anomalous thermal parameter. A subsequent refinement of its multiplicity revealed that in the crystal used for the structure solution chlorine is partially replaced by bromine (about 20%), derived by the preparation of the Grignard reagent. This replacement has been confirmed by analysing the crystal used with an EDX microprobe, which revealed the presence of both chlorine and bromine.

Note that the mutual disposition of chloride and pyridine ligands on the two palladium atoms renders the two tetrahedral nitrogen atoms chiral. The two stereogenic centers have the opposite configuration in any single molecule. Thus the obtained product is the *meso* form.

The observed geometry is the one generally found to be more stable even in the case of other bis-bridging amido complexes, although in some cases it is possible to

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observe in solution even the corresponding *syn* isomer. In the present case, this last isomer is probably highly disfavoured because of the steric interaction between the *o*-isopropyl groups.

The ^{1}H NMR spectrum (in CDCl$_3$) of the dissolved crystals showed the presence of at least six different methyl groups, but signals were not well resolved and it was not clear how many of the signals were due to the bromide substitution in the complex. When the same synthesis was repeated employing the Grignard reagent derived from benzyl chloride instead of the one from ethyl bromide a cleaner spectrum was obtained, in which four doublets of equal intensity were clearly observed [δ 0.44, *J*(H-H) = 6.76 Hz; 1.18, *J* = 6.81; 2.27, *J* = 6.90, 2.50, *J* = 6.90]. These are attributable to the eight methyl groups of the isopropyl groups, upon considering that rotation around the C-N$_{amido}$ bonds is hindered. Indeed, chirality at nitrogen is sufficient to render the two methyl groups of each isopropyl group magnetically inequivalent even if rotation around the C$_{arom.}$-C$_{isoprop.}$ bond were fast.

Three doublets of much weaker intensity (integrated as ∼ 5 % of the preceding ones) were also observed [δ 0.24, *J*(H-H) = 6.74 Hz; 1.39, *J* = 6.78; 2.44, *J* = 6.63] which are attributable to a minor product, possibly the *syn* isomer (the fourth signal is probably obscured by the more intense signals of the *anti* isomer), although data is not sufficient to prove this attribution. The signal of the protons bound to the tertiary carbon atom of the isopropyl groups could not be located. However they should be two signals with a very high multiplicity (the two methyl groups are not magnetically equivalent) and this renders them very weak.

The use of a chloride-containing reagent for the generation of the Grignard reagent also allowed us to identify the white by-product as $MgCl_2 \cdot n$ Py (Py = pyridine) since exactly the same signals in the ^{1}H NMR spectrum (δ 8.68 br and 8.62 br, in $CDCl_3$) could be obtained by dissolving $MgCl_2 \cdot n$ H_2O in pyridine, drying *in vacuo*, and redissolving the so obtained solid in $CDCl_3$.

The dimeric amido complex here reported is indefinitely stable in the air as a solid or in solution under dinitrogen and can thus represent a suitable starting material for the synthesis of more complex products.

References and Notes

†   Crystal Data: $C_{34}H_{46}Cl_2N_4Pd_2$, mw 794.48, monoclinic, space group $P2_1/c$, a= 10.866(1), b = 14.453(2), c = 11.680(2) Å , β = 105.79(1)° , V = 1765.1(4) $Å^3$, Z = 2, D_{calc} = 1.49 gcm^{-3}. The structure was solved with Patterson and Fourier methods and refined using 2121 observed reflections [I > 3σ(I)] to R= 0.025 and R_w = 0.036.

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FIGURE 1. ORTEP drawing of *anti*-[Pd(Cl)(Py)(μ-2,6-Pr^{i}C$_6$H$_3$NH)]$_2$. Thermal ellipsoids are drawn at 30 % probability level. Selected bond distances (Å) and angles (°) are: Pd-N(1) 2.060(3), Pd-N(2) 2.078(3), Pd-N(2)' 2.047(3), Pd-Cl 2.379(1), N(1)-Pd-N(2) 95.3(1), N(1)-Pd-Cl 89.5(1), Cl-Pd-N(2)' 93.6(1), N(2)-Pd-N(2)' 81.8(1), N(1)-Pd-N(2)' 176.7(1), N(2)-Pd-Cl 174.5(1).

Experimental

General Procedures.— Unless otherwise stated, all reactions and manipulations were conducted under a dinitrogen atmosphere, using standard Schlenk apparatus and cannula techniques. Solvents were dried by standard procedures and stored under dinitrogen before use. $PdCl_2Py_2$ was synthesised by dissolving $PdCl_2$ in the minimum amount of hot pyridine, cooling, and filtering the so formed precipitate. All other reagents were commercial products and were used as received. IR spectra were recorded on a Bio-Rad FTS-7 FT-IR spectrophotometer; NMR spectra were recorded on a Bruker AC 200 FT(200 MHz).

Synthesis of $[Pd(Cl)(Py)(\mu\text{-}2,6\text{-}Pr^iC_6H_3NH)]_2$. — A THF (5 ml) solution of 2,6-$Pr^iC_6H_3N(MgBr)_2$ (also containing some 2,6-$Pr^iC_6H_3NH(MgBr)$) was prepared by a modification of the method reported in ref 5, starting from bromoethane (0.715 mmol, 78 mg, 53 μl) a slight excess of magnesium (10 mg), followed, after formation of the Grignard, by addition of 2,6-$Pr^iC_6H_3NH_2$ (0.385 mmol, 63.4 mg, 67.5 μL) at 0 °C and heating at 50-55 °C for 1.5 h. The so obtained solution was added to a pyridine (15 ml) solution of $PdCl_2Py_2$ (0.350 mmol, 117.4 mg) at 0 °C. A small amount of an off-white solid precipitated and the initially yellow solution became orange. The solution was allowed to reach room temperature and, after 30 min, was filtered through a frit and the residue washed with diethyl ether (2 x 10 ml) affording a very pale yellow residue. To the filtered solution, also containing the ether washings, was added hexane (60 ml). A yellow precipitate immediately formed, which, upon standing in

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the flask under nitrogen with the mother liquors for one month separated into a white powder and orange crystals. The crystals were separated taking advantage of their much higher sedimentation rate with respect to the powder when the solution (or the following hexane washings) is stirred. The ^{1}H-NMR spectrum (in $CDCl_3$) of the first pale yellow precipitate showed no signal attributable to the 2,6-$Pr^iC_6H_3N$- fragment. Some weak signals were due to a small amount of unreacted $PdCl_2Py_2$, whereas a complex multiplet at around 8.6 ppm can be attributed to a mixture of pyridine-containing magnesim complexes, as signals in the same region were observed when a sample of dry $MgCl_2$ was treated with pyridine and the resulting suspension was first dried in vacuo and then extracted with $CDCl_3$.

X-Ray Data Collection and Refinement.— Crystals of **5** are triclinic, space group P1 (no. 2) with a = 10.218(4), b = 11.388(3), c = 17.404(3) Å, α = 96.43(2), β = 91.68(2), γ = 97.26(2)°, U = 1994(1) Å^3, Z = 2, D_{calc} = 1.33 gcm^{-3}, μ(Mo-Kα) = 5.0 cm^{-1}, F(000) = 820. Preliminary examination of a crystal, mounted on a glass fiber in a random orientation, and data collection were performed with graphite monochromatized Mo- Kα radiation (0.71073 Å) on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections, measured by the computer controlled diagonal slit method of centering. 6662 reflections were collected at room temperature using an ω-scan mode with variable

scan rate. As a check on crystal and electronic stability, three representative reflections were measured every 2 hours and showed a decay of the scattering power of the crystals during the data collection, probably due to the loss of solvent molecules, which was about 15 % on I, at the end of the data collection.

Lorentz, polarization and an empirical absorption correction were applied to the data. The structure was solved by Patterson and Fourier methods and refined with full-matrix least-squares minimizing the function $\Sigma w(|F_O|-|F_C|)^2$. Scattering factors were taken from ref. 29. Anomalous dispersion effects were included in Fc; the values for δf' and δf" were taken from ref. 30. The location of the hydride bound to the metal atom was possible by inspection of a difference Fourier map: its coordinates and displacement parameter were included in the refinement. All the remaining hydrogen atoms were considered at calculated positions (C-H 0.95 Å) and not refined. The final conventional R and R_W indicies, $\{R=[\Sigma(F_O-k|F_C|)/\Sigma F_O]$; $Rw=[\Sigma w(F_O-k|F_C|)^2/\Sigma wF_O^2]^{1/2}\}$ are 0.037 and 0.049, respectively, for 4875 observed reflections having $I > 3\sigma(I)$.

Calculations were performed on a 80486/33 computer using Personal SDP software[31]. Atomic coordinates, displacement parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.